## **PCT**

# WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT) (51) International Patent Classification 7: (11) International Publication Number: WO 00/15904 D21G 3/00 // 3/02, 3/04, B41F 15/44 A1 (43) International Publication Date: 23 March 2000 (23.03.00) PCT/FI99/00729 (21) International Application Number: (81) Designated States: AE, AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, CZ (22) International Filing Date: 9 September 1999 (09.09.99) (Utility model), DE, DE (Utility model), DK, DK (Utility model), DM, EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, (30) Priority Data: JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, 981945 10 September 1998 (10.09.98) FI MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (71) Applicant (for all designated States except US): VALMET (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian CORPORATION [FI/FI]; Fabianinkatu 9 A, FIN-00130 patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European Helsinki (FI). patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, (72) Inventors; and CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). (75) Inventors/Applicants (for US only): KIRJAVA, Jouni [FI/FI]; Jussilantie 18, FIN-36110 Ruutana (FI). RATA, Ilkka [FI/FI]; Vitsiälänkatu 4, FIN-40520 Jyväskylä (FI). **Published** VAINIO, Tommi [FI/FI]; Lummetie 13 B 15, FIN-01300 With international search report. Vantaa (FI). (74) Agent: FORSSÉN & SALOMAA OY; Yrjönkatu 30, FIN-00100 Helsinki (FI). (54) Title: DOCTOR BLADE

#### (57) Abstract

A doctor blade for use in cleaning of a roll in a paper machine. The doctor blade comprises a thermosetting plastic polymer material, whose glass transition temperature Tg is 20...30 °C higher than its operating temperature, and the resistance of the material to impacts is high.

### FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia	
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia	
AΤ	Austria	FR	France	LU	Luxembourg	SN	Senegal	
ΑU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland	
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad	
BA	Bosnia and Herzegovina	GE	Georgia	MD .	Republic of Moldova	TG	Togo	
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan	
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan	
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey	
BÇ	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago	
ВJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine	
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda	
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America	
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan	
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam	
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia	
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	zw	Zimbabwe	
CI	Côte d'Ivoire	KP	Democratic People's	NZ.	New Zealand			
CM	Cameroon		Republic of Korea	PL	Poland			
CN	China	KR	Republic of Korea	PT	Portugal			
CU	Cuba	KZ	Kazakstan	RO	Romania			
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation			
DE	Germany	LI	Liechtenstein	SD	Sudan			
DK	Denmark	LK	Sri Lanka	SE	Sweden			
EE	Estonia	LR	Liberia	SG	Singapore			

WO 00/15904 PCT/FI99/00729

#### Doctor blade

5

The invention concerns a doctor blade for a paper machine as defined in the preamble of claim 1.

Faces of rolls in a paper/board machine tend to be coated with impurities derived 10 from the process and with material from a doctor blade. Doctor blades are used in order to remove these materials from roll faces. With increasing running speeds of paper machines, it has proved to be a problem that the materials used in doctor blades do not endure these speeds of paper machines higher than 1400 metres per minute but start melting and are abraded rapidly, in which case they no longer operate in cleaning of the roll face.

Thus, an object of the present invention is to provide such a material for a doctor blade as endures higher running speeds of a paper machine and, thus, high operating temperatures.

20

15

An object of the present invention is to provide a doctor blade which, besides a high operating temperature, also possesses good mechanical strength and rigidity.

From the prior art, many doctor blades made of different materials are known, 25 including composite structures, and with respect to the prior art reference can be made, for example, to US Patent 4,549,933, published DE Patent Application 4137970, FI Patent 101,637, and to the Japanese publications 05-214696, 05-321189, and 05-132891.

30 In the US Patent 4,549,933, a doctor blade for a paper machine is described, which blade consists of a number of alternating layers of fibre and carbon fibre so that a fibre layer can consist of cotton, paper, fibreglass, or equivalent.

10

20

On the other hand, in the published *DE Patent Application 4137970*, the use of fibre-reinforced plastic, e.g., in a doctor blade is suggested, in which blade, the fibre-reinforced plastic contains 60...90 per cent by weight of polyamide-6 or of polyamide-66 and 10...40 per cent by weight of reinforcement fibres. A polyamide, which is a thermoplastic resin, is used in order to increase the thermal conductivity.

In the FI Patent 101,637, a caring doctor blade is described, which comprises a number of fibre layers as a laminate construction and whose construction comprises at least one layer of carbon fibre or at least one layer that contains a substantial proportion of carbon fibre and that contains grinding particles in direct vicinity of the carbon fibres and in which the carbon fibres are oriented substantially obliquely in relation to the direction of the longitudinal axis of the blade, favourably in the cross direction of the blade.

In the *JP publication 05-214696*, a doctor blade is described, in which polyethylene of very high molecular weight or fibre-reinforced polyethylene of very high molecular weight has been employed, which polyethylene is a thermoplastic resin.

In the *JP publication 05-321189*, a doctor blade is described which is made of a thermoplastic fibre composite material which contains 30...80 per cent by weight of polyphenylene sulphide, which is a thermoplastic resin, and 20...70 per cent by weight of either glass fibres, aramide fibres, or graphite fibres.

In the *JP publication 05-132891*, a doctor blade is described which consists of a material that contains fibreglass, in which material the fibres made of filaments have been immobilized in a resin parent material, such as epoxy resin.

As comes out from the above prior art, a number of different thermoplastic resin materials have been suggested for the matrix material. In spite of their possible good properties of resistance to heat, thermoplastic resins have not achieved commercial importance as doctor materials because of their high cost and because of their difficult workability. A thermosetting plastic from which high resistance to heat in

30

25

30

operation is expected also requires a considerably high melting-processing temperature. In practice, in commercial products, almost exclusively epoxy resins have been used.

A problem of doctor blades that comprise an epoxy matrix is their rapid wear and the resulting shorter service life. With increasing running speeds of machines the problem has become even worse. A higher speed increases the friction heat between the revolving roll and the doctor blade. The epoxy starts becoming soft and melts. The phenomenon of softening is increased by the wet conditions, for epoxy has a tendency of a certain degree to absorb water. The softening and the melting have the effect that the roll face is coated with the matrix material. This again causes changes in the properties of adhesion, separation and surface energy in the roll face, which properties are ever more critical in view of the runnability of the machine.

15 A second serious drawback of epoxy is its poor suitability for pultrusion and for similar methods by whose means continuous manufacture of doctor blades would be possible.

In view of achieving the objectives stated above and those that will come out later, the doctor blade in accordance with the invention is mainly characterized in what is stated in claim 1.

The problems that have come out in the prior art have been overcome in the present invention by means of new matrix materials. These materials are thermosetting plastic materials of which it is characteristic that their glass transition temperature Tg is sufficiently, at least about 20...30 °C, higher than the temperature to which the matrix is subjected in a situation of operation, and which materials have good impact strength. As the matrix does not come close to its Tg temperature during operation, its wear as a result of softening/melting is slower. Also, in such a case, the wear takes place in a controlled way without breaking of the tip of the blade. Controlled wear is important in order that the blade should remain sharp through its whole service life. Owing to high impact strength, the blade tip is not broken equally easily

if some material adhering to the roll face passes under the blade in a running situation.

Owing to their nature of thermosetting plastic, the materials in accordance with the present invention are suitable for being processed by means of all methods that are used with thermosetting plastics, including pultrusion, and they do not require considerable elevated temperatures, as the thermoplastic resin materials do. In the manufacture of oblong pieces, suitability for pultrusion is a highly desirable feature, because it permits continuous manufacture, in which case the overall economy of the manufacture is better and the product is of uniform quality.

In accordance with a preferred embodiment of the invention, the doctor blades are composite structures and consist of a polymer matrix and of reinforcements and of possible filler materials. The reinforcements can be conventional fibre reinforcements, such as glass, carbon or aramide fibres or structures woven out of said materials or mixtures of said fibre reinforcements. For example, a multi-layer structure can be made of such a mixture, in which structure fibreglass and carbon fibre reinforcements and the alignment of said reinforcement fibres vary/alternate in different layers.

20

25

5

10

15

In accordance with an embodiment of the invention, as the matrix material in this composite structure a new polymer material of the type of thermosetting plastic is used. This material consists of a polyester-based polyol dissolved in styrene and of polyisocyanate. In the first stage of the reaction, when the polyol component reacts with isocyanate, in a what is called chain extension reaction, urethane bonds are formed. In the second stage of the reaction, the double bonds in the polyester polyol react with the styrene as radical polymerization and cross-link a network structure typical of thermoplastic resins in the material.

30 The polymer that is formed is vinylesterurethane, which has a what is called hybrid structure in which there is both a urethane bond known from polyurethanes and a bond typical of vinylesters. The first and the second stage of the reaction take place

typically at the same time. There are several different accelerator and initiator systems by whose means the speeds of the reactions can be controlled. By their means and by means of selection of the polyester polyol it is possible to regulate the properties of the material of the doctor blade so that they become as desired in view of the purpose of use and of the processing method.

5

10

15

20

Besides the good mechanical properties of vinylesterurethane (strength, module and toughness values equal or exceed typical values of polyester/epoxy materials with high toleration of temperature) said material has an excellent toleration of temperature, the HDT temperature is up to 220 °C. Thus, it is suitable for a material for doctor blades in particular in modern high-speed paper machines, in which the surface temperatures of doctor blades become quite high.

The good mechanical properties of vinylesterurethane and its excellent toleration of chemicals are retained at elevated temperatures, and it tolerates thermal ageing well.

The raw-materials of vinylesterurethane are in solution form, and it can be processed by means of methods typical of thermosetting plastics. In the manufacture of doctor blades in accordance with the present invention, preferably pultrusion is used. Further possible methods are, for example, manufacture by means of prepregs (setting and autoclave treatment), by means of resin injection (RTM), or by means of reactive injection moulding.

In pultrusion, the speed of manufacture with vinylesterurethane is up to four times higher than with vinylesters, which lowers the cost of manufacture. The adhesion of vinylesterurethanes to different fillers is good, and, for example, ceramic and metallic fillers or cut-off-fibre reinforcements can be employed in addition to woven fibre reinforcements.

30 In accordance with an embodiment of the invention, the matrix of a composite structure is a thermosetting plastic named polyether amide (Polyether Amide Resin

= PEAR), which has been obtained from a reaction between bisoxazoline and a phenolic compound. The structure of this polymer is illustrated in a formula below describing structural units of polyether amide and structure of cross-linked polymer.

5

Bisoxazoline monomer

$$CH_{2}$$

$$OH$$

$$CH_{2}$$

$$OH$$

$$H_{2}C - O$$

$$CH_{2}$$

$$H_{2}C - N$$

$$CH_{2}$$

20

The polymer illustrated in the formula has the following good properties expressly as a material for a doctor blade:

25

- excellent thermal stability in constant operation up to 180 °C
- good adhesion to glass fibres and carbon fibres and to metals (aluminum,
   steel) and to ceramics because of its chemical structure
- good toughness (5-fold G<sub>1c</sub> value as compared with epoxy)
- 30 glass transition temperatures 225...295 °C, depending on the hardening cycle and on the material modification

#### SUBSTITUTE SHEET (RULE 26)

10

7

- the modulus of elasticity of pure non-reinforced polyether amide in the category of thermosetting plastics is very high (about 5100 MPa)
- does not contain volatile components
- low coefficient of thermal expansion (42 x 10<sup>-6</sup>/°C) as compared with other polymers.

Polyether amide is available as a solution and as a "hot melt" version. Polyether amide in solution form is, as a rule, used for the preparation of prepregs, in which case fibre reinforcements are impregnated with a solution that contains a polymer and a suitable solvent. The hot melt polymer is directly usable, for example, in a RTM method or in pultrusion, provided that the components are heated (about 160 °C) in order to lower the viscosity to a suitable level.

In the manufacture of the doctor blades in accordance with the present invention, the following techniques can be applied, which techniques are also suitable for other thermosetting plastics:

- manufacture by means of prepregs (setting and autoclave treatment)
- pultrusion
- 20 compression moulding
  - RTM (resin transfer moulding)

From the point of view of the manufacture, with polyether amide the following advantages are obtained:

25

- very low exothermic generation of heat during hardening reaction (5 times lower than with epoxies and 10 times lower than with bismaleimides)
   even thick parts are possible
- low hardening shrinkage (< 0.8 %; with epoxy about 3 %)</p>
- 30 autoclave treatments 180 °C
  - after-hardening in an oven 180...230 °C

Since polyether amide has good adhesion, among other things, to ceramics and to metals, into the matrix, if necessary, e.g., various ceramic or metallic filler particles can be mixed without considerable deterioration of the mechanical properties of the material.

5

It has been noticed that doctor blades in accordance with the present invention have a remarkably improved resistance to wear and a prolonged service life as compared with blades that contain an epoxy matrix.

Above, the invention has been described with reference to some preferred exemplifying embodiments of same only, and many modifications and variations are possible within the scope of the inventive idea defined in the following patent claims. Claims

- 1. A doctor blade for use in cleaning of a roll in a paper machine, which blade comprises a thermosetting plastic polymer material, characterized in that the glass transition temperature Tg of the polymer material is 20...30 °C higher than its operating temperature and that the resistance of the material to impacts is high.
- 2. A doctor blade as claimed in claim 1, characterized in that the polymer material is vinylesterurethane.

10

5

- 3. A doctor blade as claimed in claim 1, characterized in that the polymer material is polyether amide.
- 4. A doctor blade as claimed in claim 1, characterized in that the doctor blade contains reinforcement fibres and/or filler materials.
  - 5. A doctor blade as claimed in claim 4, characterized in that the blade has been manufactured by means of pultrusion.

## INTERNATIONAL SEARCH REPORT

International application No. PCT/FI 99/00729

			/FI 99/00/29			
A. CLAS	SIFICATION OF SUBJECT MATTER					
IPC7: I	D21G 3/00 // D21G 3/02, D21G 3/04 o International Patent Classification (IPC) or to both n	, B41F 15/44 ational classification and IPC				
	DS SEARCHED					
Minimum d	ocumentation searched (classification system followed b	y classification symbols)				
IPC7: [	D21G, B41F	· · · · · · · · · · · · · · · · · · ·				
Documentat	tion searched other than minimum documentation to th	e extent that such documents a	re included in the fields searched			
SE,DK,F	FI,NO classes as above					
Electronic d	ata base consulted during the international search (name	e of data base and, where pract	cicable, search terms used)			
WPI, PA	AJ	······································				
c. Docu	MENTS CONSIDERED TO BE RELEVANT					
Category*	Citation of document, with indication, where ap	propriate, of the relevant pa	assages Relevant to claim No.			
X	EP 0448043 A1 (PHILIPS PETROLEU 25 Sept 1991 (25.09.91), pa page 3, line 3 - line 5, ab	1,4 = 30;				
A	page 2, line 3 - line 30; pa abstract	ne 5, 2,3				
X	EP 0454404 A1 (ALBANY INTERNATION 30 October 1991 (30.10.91), line 27 - line 32, abstract	1,4				
	<del></del>					
x	WO 9904091 A1 (VALMET CORPORATION 28 January 1999 (28.01.99), line 31 - page 3, line 9, abstract	page 2,	1,3,4			
Furthe	er documents are listed in the continuation of Bo	x C. X See patent fa	amily annex.			
"A" docume	categories of cited documents: nt defining the general state of the art which is not considered particular relevance	date and not in conflict	d after the international filing date or priority with the application but cited to understand underlying the invention			
"E" erlier do	note that it is the published on or after the international filing date not which may throw doubts on priority claim(s) or which is exablish the publication date of another citation or other	"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone				
"O" documen means	reason (as specified)  Intreferring to an oral disclosure, use, exhibition or other  Introduction of the international filing date but later than	"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art				
the prior	rity date claimed	"&" document member of th	e same patent family			
Date of the	actual completion of the international search	Date of mailing of the inte	ernational search report			
22 Dece	mber 1999	<b>0 4</b> -01- 2000				
	mailing address of the ISA/	Authorized officer				
	Patent Office S-102 42 STOCKHOLM	   Mattias Arvidssor	v/ELY			
	No. +46 8 666 02 86		782 25 00			
<del></del>	A (210 (second sheet) (July 1992)	·				

RNSDOCID: <WO 0015904A1 | >

## INTERNATIONAL SEARCH REPORT

Information on patent family members

02/12/99

International application No. PCT/FI 99/00729

Patent document cited in search report		Publication date	Patent family member(s)		Publication date		
P	0448043	A1	25/09/91	CA	2031940		21/09/91
				JP	4222866		12/08/92
				US	5017643	A 	21/05/91
)	0454404	A1	30/10/91	AU	632661	В	07/01/93
				AU	7026591	A	13/02/92
				CA	2039301	A	24/10/91
				DK	73591	A	24/10/91
				EP	0454403	A	30/10/91
				FI	910481	A	24/10/91
				JP	4228695	A	18/08/92
				NO	911578	A	24/10/91
				NZ	236947	A	26/03/93
<b>_</b>				US	5110415	A	05/05/92
) )	9904091	A1	28/01/99	AU	7921898	 A	10/02/99
			. =, ==	FI	3131		04/11/97
				FI	970331		15/07/97

Form PCT/ISA/210 (patent family annex) (July 1992)

				.*	
					ų.
	,				
			•		
•					